

# ISOTOPIC RATIOS AND WEALDEN ENVIRONMENTS

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**ABSTRACT.** Isotopic methods of assessing Wealden palaeoenvironments are reviewed. Emphasis is placed on the importance of using only primary, skeletal, untransported carbonates. Recrystallization and cementation generally reduce the  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios of Wealden carbonates. Hence, while those with high  $^{13}\text{C}/^{12}\text{C}$  are likely to be marine, those with low  $^{13}\text{C}/^{12}\text{C}$  cannot be assigned to a depositional environment unless known to be primary.

Ratios from aragonitic shells of one species each of *Cassiope*, *Neomiodon*, and *Filosina*? indicate 'marine' conditions. Less certainly, marine conditions may be indicated by calcitic shells of pelecypods (one species each of *Lio-strea* and *Neomiodon*), gastropods (one species of *Paraglauconia*), and ostracods (two species of *Cypridea* and one of *Mantelliana*). Forms not assignable to 'marine' or 'fresh' water are three species of *Cypridea*, one species each of *Theriosynoecum*, *Damonella*, *Filosina*, *Unio*, *Viviparus*, and a corbulid, and two species of *Equisetites*. The new data support the transgressive models for the major Wealden clay formations.

Interpretation of transitional water temperatures from  $^{18}\text{O}/^{16}\text{O}$  ratios is unreliable. Nevertheless, values from primary aragonites in the Hastings Beds (*Neomiodon*) and Weald Clay (*Filosina*, *Cassiope*) lie in the range of modern marine molluscs from warm temperate waters. This is consistent with current opinion based on other palaeontological evidence.

AN earlier reconnaissance (Allen and Keith 1965) suggested that, in the Wealden clay formations,  $\delta^{13}\text{C}$  broadly reflects the variable depositional salinities inferred from palaeontological evidence. Subsequent work on body-fossils and trace-fossils confirms the fluctuating salinities, particularly for the Weald Clay, and the marginal environments postulated (Shephard-Thorn *et al.* 1966; Smart *et al.* 1966; Anderson 1967; Anderson *et al.* 1967; Worssam and Thurrell 1967; Thurrell *et al.* 1968; Kilenyi and N. W. Allen 1968; Dines *et al.* 1969; Kennedy and MacDougall 1969; Batten 1969; Watson 1969).

Such environments yield isotopic ratios that are so far impossible to interpret in detail (Keith and Parker 1965). This, combined with problems of Wealden diagenesis and our previous use of whole-rock samples, led us to investigate the limitations of the isotopic method more fully. In particular *Neomiodon*, with its widely ranging  $\delta^{13}\text{C}$  and varying degrees of recrystallization (Allen and Keith 1965, table 1), merited further examination.

## LIMITATIONS OF ISOTOPIC METHODS

*General.* The isotopic basis for interpreting ancient depositional environments and for distinguishing marine carbonates from  $^{13}\text{C}$ -deficient freshwater carbonates was discussed in an earlier paper (Allen and Keith 1965) and will not be repeated here, except for caveats regarding limitations on palaeosalinity estimates derived from  $\delta^{13}\text{C}$ . Measurements of isotopic compositions are reported in the standard  $\delta$ -notation, i.e. as differences of  $^{13}\text{C}/^{12}\text{C}$  (and  $^{18}\text{O}/^{16}\text{O}$ ) ratios in parts per thousand relative to those of the Chicago PDB standard, a Cretaceous belemnite:

$$\delta^{13}\text{C} = \left( \frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}} - ^{13}\text{C}/^{12}\text{C}_{\text{standard}}}{^{13}\text{C}/^{12}\text{C}_{\text{standard}}} \right) 1000.$$

Interpretation of past salinities can be based on isotopic comparisons of 'ideal' ancient carbonates with the  $\delta^{13}\text{C}$  ranges of modern carbonates (Keith *et al.* 1964). Two categories appear meaningful: 'marine' ( $\delta^{13}\text{C} > -2\text{‰}$ ) and 'freshwater' ( $\delta^{13}\text{C} < -2\text{‰}$ ), with some overlap across the arbitrary boundary. An 'ideal' sample (not easily obtained or recognized in practice) would consist of unrecrystallized carbonate formed in isotopic equilibrium with the environment to be determined and still retaining the original population of carbon (and oxygen) atoms. Complications arise mainly because other kinds of carbonate may be associated, including (a) clastic carbonates from limestones, (b) biogenic carbonates with variable or non-equilibrium carbon isotopic compositions due to vital effects (e.g. of corals, echinoids) or to localized concentrations of decomposing organic matter, (c) carbonates formed in other environments and transported to the site of deposition, or intermixed following environmental change at the depositional site, (d) carbonates formed by diagenetic recrystallization or cementation in pore-waters of variable salinity.

Any of these complications can be troublesome in samples from marginal variable-salinity environments (Keith and Parker 1965; Lloyd 1969). The present investigation relates particularly to (c) and (d). We emphasize, as did Tan and Hudson (1971), the importance of using well-preserved skeletal carbonates wherever possible, rather than whole-rock samples.

*Extraneous CaCO<sub>3</sub>*. In so far as the Weald Basin was bordered by Jurassic and Lower Carboniferous limestones (Allen 1961, 1967a), complication (a) is always possible, though no actual clasts of limestone have been confirmed in the Wealden of the Weald. The misleading influence of biogenic carbonates (allochems) transported from other environments in the same basin is illustrated by sample S8126 of Allen and Keith (1965, fig. 1 and table 1). This sample contains, among the presumably indigenous oysters, reworked bioclastic materials, both marine and non-marine (echinoid plates and spines, *Viviparus* shells, ostracod carapaces). Any salinity estimate based on the  $^{13}\text{C}/^{12}\text{C}$  ratio of the whole rock ( $-4.3\text{‰}$ ) is clearly invalid. Sediments deposited during marine transgressions across less saline environments must generally be suspect for this reason.

The complicating effects of interstitial materials and recrystallization were investigated by analysing materials from the I.G.S. borehole No. 1 at Wadhurst Park, Sussex (Anderson *et al.* 1967). Eight *Neomiodon medius* beds in the Wadhurst Clay, with shells preserved wholly or partly as aragonite, were sampled from 14.20 m to 30.25 m depth. All the shell samples gave carbon isotopic compositions in the marine range  $\delta^{13}\text{C} > -2\text{‰}$  (Table 1). All the matrices, substantially calcite, gave lower  $\delta^{13}\text{C}$  values than the shells (text-fig. 1).  $^{18}\text{O}$  varied in the same way. Thus the matrix carbonates may have originated or recrystallized in less saline environments than those of *Neomiodon*, or possibly came from organisms whose calcification processes involved different degrees of isotopic fractionation (see below). Nevertheless the matrix samples, as well as the embedded shells, seem to be marine rather than freshwater. There is only one borderline analysis (Bw 7173 matrix) with  $\delta^{13}\text{C}$  less than  $-2\text{‰}$ .

*Indigenous CaCO<sub>3</sub>*. Even carbonates demonstrably formed in the same environment

TABLE 1. Wadhurst Clay of Wadhurst Park: isotopic comparisons between aragonitic *Neomiodon medius* shells and their more calcitic matrices (I.G.S. borehole No. 1, Grid reference TQ 6325 2911).

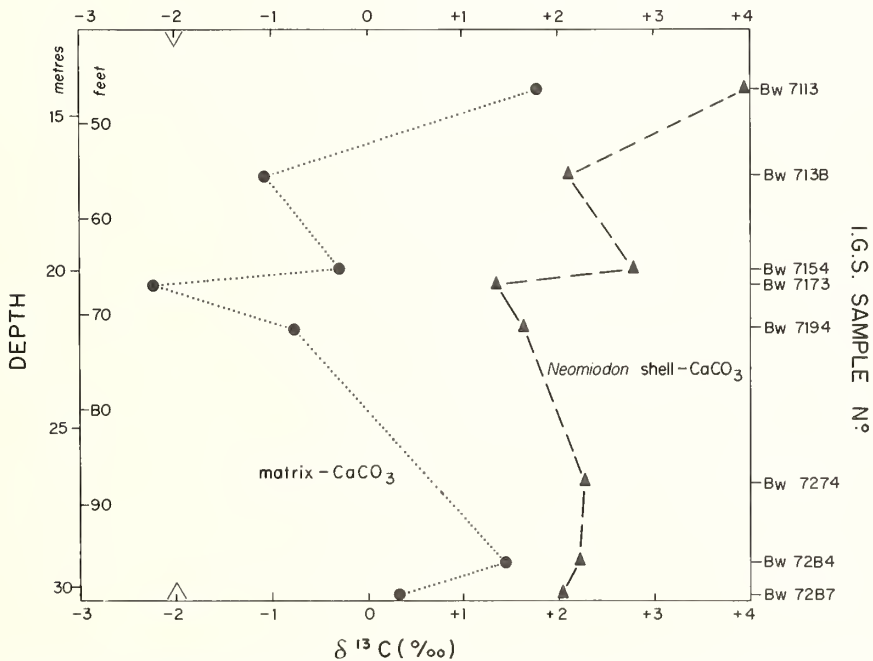
Specimen Nos.		Depth (m) in borehole	Components	Mineral (X-ray)	Isotopic analysis	
I.G.S.	Reading Univ./ Penn. St. Univ.				$\delta^{13}\text{C}(\text{‰})$	$\delta^{18}\text{O}(\text{‰})$
Bw 7113	S8129	14.20*	Shells	Aragonite	+3.95	-1.79
	68-426		Matrix	Calcite	+1.78	-3.26
Bw 7138	S8131	17.04	Shells	Aragonite	+2.10	-2.35
	68-428		Matrix	Calc. and arag.	-1.05	-3.30
Bw 7154	S8132	19.91	Shells	Arag. > calc. (tr.)	+2.78	-2.72
	68-429		Matrix	Calcite	-0.27	-5.50
Bw 7173	S8133	20.42	Shells	Arag. = calc.	+1.35	-3.00
	68-430		Matrix	Calcite	-2.19	-5.37
Bw 7194	S8134	21.79	Shells	Aragonite	+1.61	-2.24
	68-431		Matrix	Calcite	-0.78	-5.80
Bw 7274	S8135	26.77	Shells	Aragonite	+2.28	-3.53
Bw 7284	S8136	29.26	Shells	Arag. = calc.	+2.21	-2.65
	68-433		Matrix	Calcite	+1.46	-5.98
Bw 7287	S8137	30.25‡	Shells	Calc. + arag.	+2.05	-3.87
	68-434		Matrix	Calcite	+0.31	-4.76

The total thickness of Wadhurst Clay is about 67 m.

† Duplicate analyses.

\* Horizon c. 47 m below Lower Tunbridge Wells Sand.

‡ Horizon c. 4 m above Top Ashdown Pebble Bed.



TEXT-FIG. 1. Wadhurst Clay of Wadhurst Park. Carbon isotopic ratios ( $\delta^{13}\text{C}$ ) from Table 1 of separated *Neomiodon medius* ( $\blacktriangle$ ) and matrix  $\text{CaCO}_3$  ( $\bullet$ ). I.G.S. borehole No. 1.

are not necessarily straightforward to interpret isotopically. Some organisms, though living under similar conditions of salinity, temperature, etc., show different abilities to fractionate carbon and oxygen isotopes when depositing  $\text{CaCO}_3$  (Keith and Weber 1965). Decomposing organic matter adds another complication, generating  $\text{CO}_2$  with variable  $\delta^{13}\text{C}$  depending partly upon the origin of the organic matter. A further source of variation, in some cases, is isotopic fractionation between  $\text{CO}_2$  and  $\text{CH}_4$ .

Nevertheless, we show below that the  $^{13}\text{C}$ -palaeosalinities derived from Wealden carbonates are significant when considered in terms of the broad categories of 'marine' and 'freshwater' as defined on p. 608. But the transitional environments of the Wealden, with waters of highly variable  $^{18}\text{O}$ -content and salinity, offer little hope of yielding useful  $^{18}\text{O}$  palaetemperatures: the temperature effect is small compared with those of mixing and evaporation.

*CaCO<sub>3</sub> recrystallization and cementation.* Diagenetic crystallization of aragonite and calcite can modify pre-existing isotopic ratios (Gross 1964; Hodgson 1966; Stahl and Jordan 1969; Tan and Hudson 1971, and their refs.). The necessary conditions include interstitial waters with different compositions from those of the depositional environment. Recrystallization may occur soon after deposition, for example during evaporation from closed basins (Keith and Parker 1965), or on tidal flats such as sabkhas, where diagenesis occurs in the presence of supersaline porewaters. At the other extreme, transitional carbonate sediments may undergo diagenesis in the presence of low-salinity groundwater. This was apparently important in several of the samples described here.

Diagenesis affected the matrices of most of the samples from Wadhurst Park No. 1. It certainly changed all three from borehole No. 2, 200 m away (Table 2). The *Neomiodon medius* shells from this core are almost entirely calcite and there is either a little or no matrix carbonate. They give lower values of  $\delta^{13}\text{C}$  than any in borehole No. 1. This is a good example of analyses yielding no useful information

TABLE 2. Wadhurst Clay of Wadhurst Park: isotopic ratios of dominantly calcitic *Neomiodon medius* shells and matrices (I.G.S. borehole No. 2, Grid reference TQ 6308 2920 about 200 m from No. 1; horizon of top about 18.64 m above top of No. 1).

Specimen Nos.		Depth (m) in borehole	Components	Mineral (X-ray)	Isotopic analysis	
I.G.S.	Reading Univ./ Penn. St. Univ.				$\delta^{13}\text{C}(‰)$	$\delta^{18}\text{O}(‰)$
Bw 7353	S8138 68-435	16.15	Shells	Calc. > arag.	-5.17	-7.87
Bw 7377	S8139 68-436	16.36	Shells Matrix	Calcite Calcite	-2.29 -0.39	-3.46 -4.68
Bw 7385	S8140 68-437	16.43*	Shells Matrix	Calc. > arag. Calcite	-3.37 { -3.25† -0.81 { -0.91† -0.72†	-5.79 { -5.70† -2.78 { -2.79† -2.77†

\* Horizon c. 30.6 m below Lower Tunbridge Wells Sand and c. 36.4 m above Top Ashdown Pebble Bed.

† Duplicate analyses.

about an original depositional environment. The shells are recrystallized, they give lower  $\delta^{13}\text{C}$  ratios than their matrices (cf. borehole No. 1) and they straddle the arbitrary division ( $-2\text{‰}$ ) between marine and freshwater shells.

Four analyses of *Neomiodon*-rock previously published (Allen and Keith 1965, table 1) probably reflect the combined influences of calcite cementation and the diagenetic change of aragonite to calcite. The rocks are shelly calcareous sandstones ('Tilgate stone'), comprising quartz clasts and calcite valves cemented with clear calcite (S8112, S8113, S8115, S8118). All give low  $\delta^{13}\text{C}$  ( $-8.3$  to  $-4.7\text{‰}$ ). Three other samples (S8109-S8111) are quartz-free, virtually uncemented, and their *Neomiodon medius* shells retain some aragonite. All yield substantially higher  $\delta^{13}\text{C}$  values ( $-1.3$  to  $+0.2\text{‰}$ ). Apparently some of the  $\delta^{13}\text{C}$  variation previously attributed to a wide salinity tolerance in *Neomiodon* arises from the postdepositional production of calcite through the action of groundwater.

In general, therefore, cementation or recrystallization reduced the  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios of the Wadhurst sediments. The same is true of the Weald Clay. Prentice (1969, pp. 3-4) describes Weald Clay cycles and concludes that they record upward-decreasing salinities which are parts of a general salinity series *Cassiope*  $\rightarrow$  'Cyrena' [presumably *Filosina*]  $\rightarrow$  'Paludina' [presumably *Viviparus*]  $\rightarrow$  ostracods  $\rightarrow$  *Equisetites*. This series has been largely confirmed. During the course of our work a small cycle at Ewhurst, high in the Weald Clay (Table 3), showed how effectively recrystallization of shell aragonite could destroy original isotopic evidence.

Shells of Wealden age from Germany show the same kind of variation. Marine *Cucullaea*, collected (with the ammonite *Platylenticeras*) from the basal Valanginian of Sachsenhagen (1 m above the Wealden), are entirely calcite, though originally aragonite (Hall and Kennedy 1967). Their  $\delta^{13}\text{C}$ - and  $\delta^{18}\text{O}$ -values are low ( $-2.3$  and  $-8.5\text{‰}$ ), i.e. spuriously 'freshwater' (samples S8128/68-444). On the other hand *Neomiodon* (S8161) and *Paraglauconia* (S8162) from the underlying Wealden, though similarly recrystallized to calcite, have carbon ratios ( $\delta^{13}\text{C} = -1.32$  and  $-1.66\text{‰}$  respectively) in the arbitrary marine range.

#### HASTINGS BEDS

*Salinity.* Palaeontological evidence suggests that, of the two major Wealden subdivisions, the lower (or Hastings Beds) records a generally narrower range of salinities. Prior to our isotopic work, no macrofossils of near-marine aspect were known, nor any microfossils, though foraminifera had been alluded to in general terms (Anderson *et al.* 1967, p. 175). Salinity variations had, however, long been suspected and sought (e.g. Allen 1962, p. 226). The basis was the observed antipathy, on single lamination surfaces, between swarms of *Neomiodon* (Casey 1955*b*) and the other fossil assemblages. The latter, hinting at rather fresher water, include stoneworts (one species of *Circonitella*: Watson 1969), liverworts (two species of *Hepaticites*: *op. cit.*), probable liverworts preserved *in situ* (*op. cit.*, fig. 13), horsetails *in situ* (two or three species of *Equisetites*), and dominant *Viviparus*, *Physa*, *Unio*, or *Cypridea* spp. (Anderson *et al.* 1967). *Neomiodon* was thought to have lived in more brackish conditions. Its German contemporaries were already known to consort with unequivocally brackish fossils (Allen 1967*a*, p. 60). The new isotopic evidence places *Neomiodon*

TABLE 3. Small cycle in upper Weald Clay, laneside ditch, 1 km ESE. parish church, Ewhurst, Surrey (TQ 101 401).

Subsample Nos.		Stratigraphy	Thick- ness (m)	Component analysed	Palaeontological salinity	Isotopic analysis		Environmental category
Reading Univ.	Penn. St. Univ.					$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	
S8155	71-153	Large- <i>Viviparus</i> limestone (scattered <i>Lepidotus</i> scales)* Laminated clays	0.05	<i>Viviparus sussexensis</i> shells (calcite)	Freshwater	-5.22	-4.41	Indeterminate
S8154	71-152	Pebbly glauconitic calcareous <i>Filosina</i> †- sandstone forming isolated runnel- casts (scattered clay pellets to 1.2 × 1.6 cm, ostracods, † large- <i>Viviparus</i> , and <i>Lepidotus</i> scales)	1.00 0.01	— <i>Filosina gregaria</i> shells (calcite)	— Brackish water	— -5.04	— -5.77	— Indeterminate

\* Horison: I.G.S. Bed 8b of Thurrell *et al.* 1968.

† Disarticulated valves, many broken.

----- Erosion surface -----

*medius* squarely in our 'marine' category. This recalls Tan and Hudson's work (1971) showing that well-preserved aragonitic shells of *Neomiodon* from the Hebridean Middle Jurassic have a 'marine' range of  $\delta^{13}\text{C}$ .

The notion that salinity exerted a major control arose from the theory that the Hastings clays were broadly transgressive and the sandstones regressive (Allen 1959). Accepting that these movements were caused by the sea and physically connected with it, the basal strata of each clay formation should record rising salinities (Allen 1959, p. 342) and the top sands of each arenaceous formation falling salinities. This could explain the marked antipathy between basal reedswamp and burrowed beds (Allen 1962) and the absence from the Wealden of strictly freshwater ostracod genera. If the lowest salinities were normally achieved during deposition of the regressive sands then such ostracods are the least likely to have been preserved (Anderson 1967, *in litt.*).

*Salinities from Wadhurst Clay.* Previous isotopic analyses of aragonite-bearing *Neomiodon medius* from the ?transgressive basal Wadhurst (S8109-S8111, in Allen and Keith 1965) strengthened the idea that, as the waters rose, their salinities rose too ( $\delta^{13}\text{C} = -1.3$  to  $+0.2\text{‰}$ ).

Salinity fluctuations in the type-area of Wadhurst Park (I.G.S. boreholes Nos. 1-3) were independently investigated by Anderson, using ostracods (in Anderson *et al.* 1967). Less saline and more saline episodes were recognized, assuming that the former are recorded by *Cypridea*-dominated faunas and the latter by 'non-*Cypridea*' faunas (*Theriosynoecum*, *Mantelliana*, *Rhinocypris*, Darwinulids, *Dicrorygma*). We attempted to test the distinction by analysing *C. laevigata* carapaces ('the nearest to a freshwater ostracod we have in the Purbeck-Wealden') and *T. allenii* ('strongly brackish to marine'), kindly prepared and so interpreted by Professor F. W. Anderson from the Westfield I.G.S. borehole (TQ 8204 1614, Shephard-Thorn 1971). *C. laevigata* gave a freshwater ratio ( $\delta^{13}\text{C} = -4.4\text{‰}$ ) but its carapaces enclosed much secondary calcite. Those of *T. allenii* were too few for analysis; associated aragonitic fragments (molluscan?) gave a marine ratio ( $\delta^{13}\text{C} = +0.48\text{‰}$ ).

Our new analyses of well-preserved *Neomiodon medius* (Table 1) support the contention that the Wadhurst waters became saline at times. Rejecting isotopic ratios based on subordinate or no aragonite, we have eight horizons scattered over 16 m of the local 67-m succession. All their  $\delta^{13}\text{C}$  values range from  $+1.4\text{‰}$  (shell carbonate half-aragonite) to  $+4.0\text{‰}$  (carbonate wholly aragonite) and thus fall into the 'marine' category.

*Salinities from Grinstead Clay.* Comparison of the base (?transgressive) of this formation with that of the Wadhurst Clay raises an interesting ecological question. Strikingly similar in physical sedimentology, they differ in that the Grinstead base was not colonized widely (if at all\*) by aquatic horsetails (Allen 1962, p. 236-7). Probably it also contains a richer and more abundant ostracod fauna. Perhaps more saline water explains both features.

\* Rootlets (i.e. downward-branching tubules with carbonaceous linings) are found rarely and locally, but not as commonly as previously supposed, when animal burrows were mistaken for them (Allen 1959, 1960). The few true rootlets do not visibly originate at this level, but probably from rhizomes higher up, e.g. the mid-Grinstead *Equisetites* soil bed (Gallois 1963) 6-7 m above.

TABLE 4. Palaeontological and isotopic analyses of ostracod carapaces (calcite) near base of Grinstead Clay at Philpots Quarry, West Hoathly, Sussex (TQ 355 322).

Source of material		Palaeontological analysis		Isotopic analysis		
Height above TLTWPB‡	Lamina	Microfauna	Salinity	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	Environmental category
2.90 m		<i>Mantelliana phillipsiana</i> dominant	Relatively high		Not analysed	
1.43 m to 1.32 m	C	<i>Cypridea recta tilsdenensis</i> and <i>C. bispinosa suttin-gensis</i> predominantly (S8145/71-151C)	Relatively low	+0.58* -0.13†	-2.39* -2.46†	Marine?
	B	<i>M. phillipsiana</i> , <i>Cypridea recta tilsdenensis</i> , <i>C. bispinosa suttin-gensis</i> (S8144)	Intermediate		Not analysed	
	A	<i>Mantelliana phillipsiana</i> mainly (S8143/71-151S)	Relatively high	+0.05	-2.86	Marine?
1.01 m		<i>Theriosynoecum alleni</i> dominant (S8146)	Relatively high		Not analysed	

Sample nos. given in microfauna column (Reading Univ./Penn. State Univ.)

\* Treated 3 days in  $\text{H}_2\text{O}_2$  to remove organic matter.

† Treated 3 days in sodium hypochlorite (5% solution).

‡ Top Lower Tunbridge Wells Pebble Bed.

Our new isotopic results are compared with Professor Anderson's palaeontological analyses in Table 4. Laminae A, B, and C were half-millimetre partings of closely packed ostracod carapaces, many articulated, separated by black clay (1-5 mm) with sparse carapaces. The higher salinities predicted by the transgressive model seem confirmed. However, the  $^{13}\text{C}$  technique cannot apparently resolve all the palaeontological differences recognized by Professor Anderson and for the isotopic interpretation we assume that the ostracod calcite was primary. We have been unable to confirm the last assumption. But it appears to be strengthened, as Dr. J. D. Hudson points out, by our Hastings ostracods generally giving  $^{18}\text{O}$  ratios that could be depositional (see below), like the aragonitic but unlike the recrystallized shells.

Shells of '*Tornatella*', *Neomiodon*, *Unio*, *Viviparus*, etc., from the succeeding clays prove to contain little or no aragonite. We therefore have no Grinstead samples of primary molluscan carbonate, and isotopic analysis does not provide reliable estimates of salinity. A new analysis of *Unio subtruncatus* shell (subsample 71-161 from Philpots Quarry, West Hoathly, Sussex) gave no aragonite,  $\delta^{13}\text{C} = -7.08\text{‰}$  and  $\delta^{18}\text{O} = -8.30\text{‰}$ .

*Temperature.* No reliable temperatures can be calculated because the oxygen isotopic compositions of the marginal waters are unknown and the temperature effect is small relative to those of mixing and evaporation (Keith and Parker 1965; Lloyd 1969). Nevertheless, the  $\delta^{18}\text{O}$  variation of aragonitic *Neomiodon* (-3.9 to -1.8‰)



is generally within the range of modern marine mollusc shells from warm temperature waters (Keith *et al.* 1964). This agrees well with recent opinions concerning the English Purbeck-Wealden ostracods ('water temperatures . . . suggest a Mediterranean type climate': Professor F. W. Anderson 1970, *in litt.*), molluscs ('warm temperate': late W. J. Arkell), land reptiles ('subtropical': Dr. W. E. Swinton 1970, *in litt.*), reptiles generally ('warm temperate': Dr. K. A. Kermack 1970, *in litt.*), and flora ('warm temperate . . . alternations of wet and dry periods . . . drought over some months . . . normal': Professor T. M. Harris 1970, *in litt.*). Bowen (1966), on the basis of  $\delta^{18}\text{O}$  values from marine sediments, quoted temperatures of 17.4 °C to 22.1 °C for the contemporary Neocomian seas of the Hautes Alpes, 800 km SSE. of the Weald.

#### WEALD CLAY

*Salinity.* More drastic variations in environment are indicated by the Weald Clay fossils above the Horsham Stone. Palaeontologically, freshwater is suggested by numerous beds with *Chara*, *Equisetites*, *Cypridea*, *Viviparus*, and *Unio*, often as largely separate associations. Marine or near-marine conditions are recorded by at least three thin bands variously containing *Ostrea*, *Nemocardium*, *Mytilus*, *Gervillia*, *Corbula*, *Filosina*, *Melanopsis*, *Cassiope*, *Paraglauconia*, echinoids, cirripedes, foraminifera, *Ophiomorpha*, etc. (see references on p. 607). Other horizons are dominated by only one or two of these genera (Kennedy and MacDougall 1969) or by non-*Cypridea* ostracods (Anderson 1963, 1968), suggesting less stable environments. Of the ecological factors, fluctuating salinity may have been important, perhaps limiting.

Our previous isotopic reconnaissance (Allen and Keith 1965) did little more than support the broad picture. *Theriosynoecum fittoni* (identified subsequently by Professor F. W. Anderson as dominant in sample S8127) may have lived in freshwater, as deduced by Kilenyi and N. W. Allen (1968, pp. 158, 162). If confirmed, this might contrast with the Wadhurst species of the same genus, for which brackish to marine conditions are possible (cf. Tan and Hudson 1971, table 3). Unfortunately our carapaces of *T. fittoni* contained some secondary calcite; and the evidence concerning *T. alleni* is indirect, being based on associated 'marine' shell fragments.

Near the arbitrary freshwater/marine boundary our original results (1965) were suspect owing to the recrystallization of *Filosina*-aragonite to calcite (S8120) and to the choice of whole-rock analysis for the oyster bed (S8126). Subsequent determinations of  $\delta^{13}\text{C}$  for the oyster-carbonate alone gave  $\delta^{13}\text{C} = +1.16\text{‰}$  (Table 5).

*Skeletal CaCO<sub>3</sub>.* Like their predecessors, the Weald Clay fossil carbonates were commonly recrystallized after deposition (Table 5 and text-fig. 2).

For originally aragonitic shells, and assuming that recrystallization of aragonite generally yielded calcite, the proportion of aragonite may be used to judge whether the original isotopic ratios may have been retained. Unfortunately, we were unable to establish any independent non-isotopic criteria for identifying the primary, unrecrystallized calcite of ostracods, oysters, etc. Such criteria may eventually be developed. Thus preliminary studies show differences in the cathodoluminescence of organic and diagenetic carbonates, and most ostracod valves have a three-layered structure (formed by the calcitization of a chitinous envelope) which is frequently

TABLE 5. New isotopic and palaeontological analyses of skeletal CaCO<sub>3</sub> from the Weald Clay (Weald) and upper Wealden Shales (Isle of Wight), in probable stratigraphical order.

Reading Univ./I.G.S.	Subsample Nos.	Locality	Palaeontological analysis		Mineral (X-ray)	Isotopic analysis		Environmental category
			Identity	Salinity		$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	
S8158	71-156	Isle of Wight Sandown	<i>Liosorea ?distorta</i> <i>Filosina gregaria</i>	from same bedding surface	Calcite Calcite	+1.16 -7.07	-2.90 -5.32	Marine?
S8157	71-155							
S8155	71-153	Weald Ewhurst, Surrey	<i>Viviparus sussexensis</i> <i>Filosina gregaria</i>	f br	Calcite Calcite	-5.22 -5.04	-4.41 -5.77	Marine?
S8154	71-152							
S8151	68-352							
S8152	71-150A	Leigh, Surrey	<i>Equisetites burcharadi</i> (in situ) <i>Cypridea rotundata</i> <i>Cypridea valdensis</i> <i>Damonella pygmaea</i>	56% 21% 23% * f*	Calcite	-7.29	-2.90	Freshwater?
S8156/ W1423-24 (I.G.S.)	71-154	Worthingham, Surrey	<i>Filosina? membranacea</i>	br	Arag.	-1.01	-2.63	Marine
S8150	68-355F	Capel, Surrey	Corbulid† <i>Cassiope</i>	br?	Calcite	-8.55	-9.28	Marine?
S8147	68-346	Worthingham, Sussex		br	Calcite > tr. arag.	-0.71	-5.82	
S8149	68-348B	Capel, Surrey	<i>Cassiope</i>	br	Arag. > calc.	-1.20	-4.63	Marine
S8148	68-348A	"	<i>Cassiope</i>	br	Calc. > arag.	-2.85	-6.46	

destroyed by recrystallization. Our Weald Clay ostracods, moreover, show  $^{18}\text{O}$  ratios that could be depositional, as in the Hastings Beds (pp. 614–15).

As for the Hastings Beds, semiquantitative estimates of aragonite:calcite ratios were made from X-ray diffraction patterns. Samples in which aragonite is dominant are depicted as black rectangles in text-fig. 2. The two genera represented (*Filosina*?, *Cassiope*) deserve particular attention as potential indicators of the environment of deposition. Both appear, like *Neomiodon*, to have been 'marine'.

Shells of the freshwater mollusc *Viviparus*, presumably originally aragonite, are now calcite, and do not provide a basis for judging whether their present isotopic composition is due mainly to conditions of deposition or diagenesis. As pointed out above, calcite shells of *Filosina* (subsamples 71–152 and 71–155 belong to another species) are sometimes deficient in  $^{13}\text{C}$  and thereby isotopically indistinguishable from recrystallized freshwater shells such as *Viviparus* (71–153).

Because of the non-preservation of aragonitic *Viviparus* shells (including those of Allen and Keith 1965) it is still not possible either to support or refute

## KEY TO TABLE 5

\* Identified, counted, and interpreted by Professor F. W. Anderson (some carapaces 2- or 3-layered, many infilled micrite or drusy calcite).

† Provisionally identified by Dr. R. Casey (life assemblage of articulated shells, young and old).

‡ Early post-mortem cement?

*f* = freshwater, *br* = brackish water, *m* = marine.

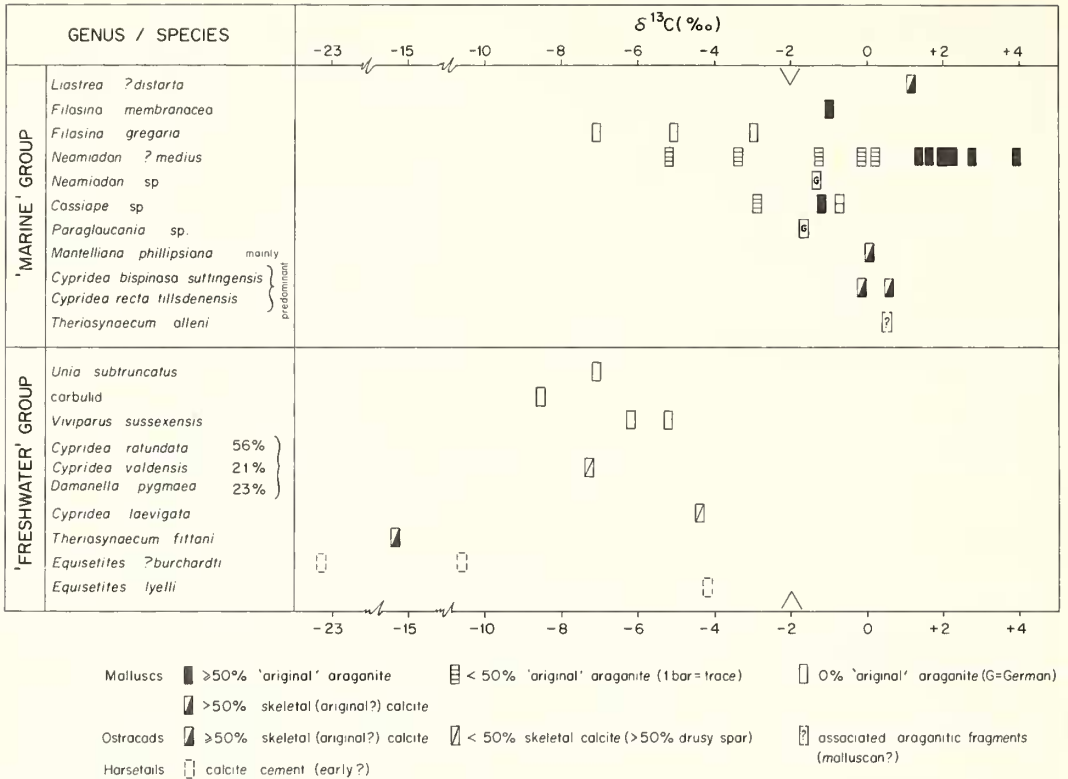
**Bold type** indicates samples in which the analysed carbonate was mostly aragonite (primary?).

*Details of localities*

- S8158 } Seacliff, Sandown, Isle of Wight (SZ 620 853).  
 S8157 }  
 S8155 } 1 km ESE. parish church, Ewhurst, Surrey (TQ 101 401).  
 S8154 }  
 S8151 Vann Lane Brickworks, Hambledon, Surrey (SU 974 374).  
 S8152 Bunce Common, Leigh, Surrey (TQ 205 466).  
 S8156/W1423-3 I.G.S. Warlingham boring No. 1, Surrey (TQ 349 571).  
 S8150 Clock House Brickworks, Capel, Surrey (TQ 176 384).  
 S8147 Graylands Brickworks, Warnham, Sussex (TQ 173 345).  
 S8149 } Clock House Brickworks, Capel, Surrey (TQ 176 384).  
 S8148 }

*Stratigraphical horizons*

- S8158 } Probably that of Bristow 1889, 15, top line.  
 S8157 }  
 S8155 } 1 m below I.G.S. Bed 8b, *c.* 90 m (300 ft) below top of Weald Clay (Thurrell *et al.* 1968).  
 S8154 }  
 S8151 I.G.S. Bed 7g?, *c.* 120 m (400 ft) below top of Weald Clay (Thurrell *et al.* 1968; Kennedy and MacDougall 1968).  
 S8152 180 m (600 ft) below top of Weald Clay (Professor F. W. Anderson *in litt.*).  
 S8156/W1423-4 Subjacent to I.G.S. Bed 5, *c.* 115 m (377 ft) below top of Weald Clay (Worssam and Ivimey-Cook 1972, pp. 22, 30, 64).  
 S8150 *c.* 10.7 m (35 ft) above *Cassiope* Bed (S8148–9), beneath Upper Rootlet Bed (Mr. J. D. S. MacDougall).  
 S8147 *c.* 4.9 m (16 ft) above Gossops Green Pebble Bed, *c.* 91 m (300 ft) above Horsham Stone (*c.* 150 m (500 ft) above Weald Clay base).  
 S8149 } Just above Gossops Green Pebble Bed, *c.* 82 m (270 ft) above Horsham Stone (*c.* 146 m (480 ft) above  
 S8148 } Weald Clay base (Mr. J. D. S. MacDougall *in litt.*)).



TEXT-FIG. 2. Wealden as a whole. Provisional environmental classification of fossils based on  $\delta^{13}\text{C}$  of separated shells and carapaces. (Estimated relative frequencies of species in the ostracod faunas were supplied, with samples, by Professor F. W. Anderson. Two molluscan samples, labelled 'G', came from N. Germany.)

suggestions that some viviparids tolerated brackish or marine conditions in the Purbeck-Wealden.

*Temperature.* As concluded for the Hastings Beds, the  $\delta^{18}\text{O}$  variation of the aragonite shells lies in the range of modern warm temperate molluscs and this is consistent with recent opinion based on other palaeontological evidence.

CONCLUSIONS

(1) Whole-rock isotopic analyses are unsatisfactory for environmental studies of marginal (transitional) sediments. Primary, skeletal, untransported carbonates only should be used. This means in practice only unfragmented articulated aragonitic material.

(2) One species each of *Filosina?* and *Cassioppe* (from the Weald Clay) and of *Neamiadon* (Hastings Beds) are confirmed as 'marine'.

(3) Conversion to, and/or cementation with, calcite commonly reduces the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of Wealden molluscan shells. 'Marine' molluscs can therefore

appear as 'freshwater', isotopically indistinguishable from truly freshwater shells. This was examined closely for *Neomiodon medius*, having been misinterpreted earlier (Allen and Keith 1965) as resulting from the organisms' wide salinity tolerance.

(4) Wealden skeletal carbonates giving high  $\delta^{13}\text{C}$  are therefore likely to be 'marine', even if secondary (e.g. German *Neomiodon* and *Paraglauconia*).

(5) Skeletal carbonates yielding low  $\delta^{13}\text{C}$  cannot be attributed to any environment unless shown to be primary. Freshwater molluscs now recrystallized to calcite (*Unio*, *Viviparus*) are unrecognizable as such on an isotopic basis alone.

(6) Skeletal carbonate which was originally all, or nearly all, calcite (e.g. ostracod carapaces, oyster shells) should be treated with caution. Recrystallization may or may not have occurred. At present there are no certain criteria for recognizing primary calcite or for distinguishing it from secondary calcite, though there are petrological and isotopic grounds for optimism with the ostracods.

(7) Ignoring this, and assuming that any recrystallization would have reduced their  $^{13}\text{C}$ -ratios ((3) above), one species of the ostracod *Mantelliana* and two species of *Cypridea* might be marine. Other species of *Cypridea* may be freshwater, but this cannot be confirmed isotopically until their calcite is proved to be primary.

(8) Areal distributions of horsetail-reedswamp growing in similar substrates and water-depths were possibly controlled by salinity. But the source of the  $^{13}\text{C}$ -deficient calcite cementing the plants in their growing positions is not known, nor when it was precipitated. Where plants are absent, the  $^{13}\text{C}$ -rich ostracod carapaces appear.

(9) New evidence supports the transgressive models for the major Hastings clay formations (Allen 1967*b*, fig. 1) in that the Wadhurst and Grinstead Clays are there seen as deposited in waters more liable to saline influxes than the intervening sands. Later, during Weald Clay times, the salty invasions became more frequent and extensive, so that not only many muds but also some sands were laid down in conditions more saline than any of the Hastings Beds.

(10) Unequivocal palaeotemperatures cannot be deduced from Wealden carbonates. Nevertheless the aragonitic shells yield  $^{18}\text{O}$ -'palaeotemperatures' broadly consistent with warm temperate-subtropical conditions, as deduced from the palaeobotanical and palaeozoological evidence.

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## REFERENCES

- ALLEN, P. 1959. The Wealden environment: Anglo-Paris basin. *Phil. Trans. roy. Soc.*, **B**, **242**, 283-346.  
 — 1960. Geology of the Central Weald: a study of the Hastings Beds. *Geol. Assoc. Centenary Guide*, No. **24**.  
 — 1961. Strand-line pebbles in the mid-Hastings Beds and the geology of the London uplands. Carboniferous pebbles. *Proc. Geol. Assoc.* **72**, 271-285.  
 — 1962. The Hastings deltas: recent progress and Easter field meeting report. *Proc. Geol. Assoc.* **73**, 219-243.

- ALLEN, P. 1967a. Origin of the Hastings facies in northwestern Europe. *Proc. Geol. Assoc.* **78**, 27-106.
- 1967b. Strand-line pebbles in the mid-Hastings Beds and the geology of the London uplands. Old Red Sandstone, New Red Sandstone and other pebbles. *Proc. Geol. Assoc.* **78**, 241-276.
- and KEITH, M. L. 1965. Carbon isotope ratios and palaeosalinities of Purbeck-Wealden carbonates. *Nature*, **208**, 1278-1280.
- ANDERSON, F. W. 1963. In WORSSAM, B. C. 1963, 16-19.
- 1966a. In SHEPHARD-THORN, E. R. *et al.* 1966, 82-88.
- 1966b. New genera of Purbeck and Wealden Ostracoda. *Bull. Brit. Mus. (Nat. Hist.) Geol.* **11** (9), 435-446.
- 1967. Ostracods from the Weald Clay of England. *Bull. geol. Surv. Gt. Brit.*, No. **27**, 237-269.
- 1968. In THURRELL, R. G. *et al.* 1968, 27-30.
- BAZLEY, R. A. B. and SHEPHARD-THORN, E. R. 1967. The sedimentary and faunal sequence of the Wadhurst Clay (Wealden) in boreholes at Wadhurst Park, Sussex. *Bull. geol. Surv. Gt. Brit.*, No. **27**, 171-235.
- ARKELL, W. J. 1947. The geology of the country around Weymouth, Swanage, Corfe, and Lulworth. *Mem. geol. Surv. Gt. Brit.*
- BATTEN, D. J. 1969. Some British Wealden megaspores and their facies distribution. *Palaeontology*, **12**, 62-67.
- BOWEN, R. 1966. *Palaeotemperature Analysis*. 265 pp. Amsterdam.
- BRISTOW, H. W. 1889. The geology of the Isle of Wight (2nd edition, revised and enlarged by REID, C. and STRAHAN, A.). *Mem. geol. Surv. Gt. Brit.*
- CASEY, R. 1955a. The pelecypod family Corbiculidae in the Mesozoic of Europe and the Near East. *J. Wash. Acad. Sci.* **45**, 366-372.
- 1955b. The Neomiodontidae, a new Family of the Arcticoacea (Pelecypoda). *Proc. mal. Soc. Lond.* **31**, 208-222.
- DINES, H. G., BUCHAN, S., HOLMES, S. C. A. and BRISTOW, C. R. 1969. Geology of the country around Sevenoaks and Tonbridge. *Mem. geol. Surv. Gt. Brit.*
- GALLOIS, R. W. 1963. In *Sum. Progr. geol. Surv. Gt. Brit. for 1962*, 39.
- GROSS, M. G. 1964. Variations in  $O^{18}/O^{16}$  and  $C^{13}/C^{12}$  ratios of diagenetically altered limestones in the Bermuda Islands. *J. Geol.* **72**, 170-194.
- HALL, A. and KENNEDY, W. J. 1967. Aragonite in fossils. *Proc. roy. Soc.*, **B**, **168**, 377-412.
- HODGSON, W. A. 1966. Carbon and oxygen isotope ratios in diagenetic carbonates from marine sediments. *Geochim. Cosmochim. Acta*, **30**, 1223-1233.
- KEITH, M. L., ANDERSON, G. M. and EICHLER, R. 1964. Carbon and oxygen isotopic composition of mollusk shells from marine and fresh water environments. *Geochim. Cosmochim. Acta*, **28**, 1757-1786.
- and PARKER, R. H. 1965. Local variation in  $^{13}C$  and  $^{18}O$  content of mollusk shells and the relatively minor temperature effect in marginal marine environments. *Marine Geol.* **3**, 115-129.
- and WEBER, J. N. 1965. Systematic relationships between carbon and oxygen isotopes in carbonates deposited by modern corals and algae. *Science*, **150**, 498-501.
- KENNEDY, W. J. and MACDOUGALL, J. D. S. 1969. Crustacean burrows in the Weald Clay (Lower Cretaceous) of south-eastern England and their environmental significance. *Palaeontology*, **12**, 459-471.
- KILENYI, T. I. and ALLEN, N. W. 1968. Marine brackish bands and their microfauna from the lower part of the Weald Clay of Surrey and Sussex. *Palaeontology*, **11**, 141-162.
- LLOYD, R. M. 1969. A palaeoecological interpretation of the Caloosahatchee Formation, using stable isotope methods. *J. Geol.* **77**, 1-25.
- MACDOUGALL, J. D. S. and PRENTICE, J. E. 1964. Sedimentary environments of the Weald Clay of south-western England. In VAN STRAATEN, L. M. J. U. (ed.), *Developments in Sedimentology*, 1: Deltaic and shallow marine deposits, 257-263. Amsterdam.
- PRENTICE, J. E. 1969. Sediments: past, present and future. *Inaugural Lecture, University of London, King's College*, 1-8.
- SHEPHARD-THORN, E. R., SMART, J. G. O., BISSON, G. and EDMONDS, E. A. 1966. Geology of the country around Tenterden. *Mem. geol. Surv. Gt. Brit.*
- 1971. In *I.G.S. Annual Report for 1969*, 20.
- SMART, J. G. O., BISSON, G. and WORSSAM, B. C. 1966. Geology of the country around Canterbury and Folkestone. *Mem. geol. Surv. Gt. Brit.*

- STAHL, W. and JORDAN, R. 1969. General considerations on isotopic palaeotemperature determinations and analyses on Jurassic ammonites. *Earth planet. Sci. Lett.* **6**, 173-178.
- TAN, F. C. and HUDSON, J. D. 1971. Isotopic composition of carbonates in a marginal marine formation. *Nature phys. Sci.* **232**, 87-88.
- THURRELL, R. G., WORSSAM, B. C. and EDMONDS, E. A. 1968. Geology of the country around Haslemere. *Mem. geol. Surv. Gt. Brit.*
- WATSON, J. 1969. A revision of the English Wealden flora, I. Charales-Ginkgoales. *Bull. Br. Mus. nat. Hist. (Geol.)* **17**, No. 5.
- WORSSAM, B. C. 1963. Geology of the country around Maidstone. *Mem. geol. Surv. Gt. Brit.*
- 1965. In *Summ. Progr. geol. Surv. Gt. Brit. for 1964*, 46-47.
- and IVIMEY-COOK, H. C. 1972. The stratigraphy of the Geological Survey borehole at Warlingham, Surrey. *Bull. geol. Surv. Gt. Brit.*, No. **36**, 1-146.
- and THURRELL, R. G. 1967. Field meeting to an area north of Horsham, Sussex. *Proc. Geol. Assoc.* **67**, 263-272.

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